

THE KINETICS OF REACTIONS OCCURRING IN THE UNPOLLUTED TROPOSPHERE, I

FORMULATION OF THE REACTION MECHANISM

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A reaction mechanism called background model has been formulated which is intended to describe the photochemistry in the "unpolluted" troposphere i.e. in the relatively clean atmosphere not exposed to the direct perturbation from local emitting sources. The mechanism consists of 48 chemical reactions, including 12 photochemical steps, and 12 emission and deposition processes. Selection of the reactions included in the scheme has been based on competitive kinetic consideration using recent kinetic and photochemical parameters. The model has been applied to the computation of diurnal concentration profiles of the trace pollutants of the troposphere.

Introduction

A great deal of efforts has been directed toward the elucidation of the mechanism of photochemical smog formation and modelling the photochemistry of highly polluted atmosphere [1–4].

On the other hand, relatively little attention has been paid to the photochemistry of the unpolluted troposphere.

Levy's hypothesis on the role of free radicals in the troposphere [5, 6] and Crutzen's discovery of the formation and photochemical destruction of ozone in the unpolluted lower atmosphere [7, 8] initiated studies of the tropospheric photochemistry which resulted in the formulation of photochemical models for the global troposphere [9, 10] and for the marine atmosphere [11, 12].

The reason for the moderate attention received in the past by the photochemistry of unpolluted lower atmosphere was at least in part the scarcity of information on emission and concentration data of minor tropospheric constituents as well as the paucity of accurate kinetic data for photochemical and thermal elementary chemical reactions. However, a number of concentration measurements were made in the lower atmosphere recently and some global emission data both from natural and from anthropogenic sources became available.

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Furthermore, excellent critical compilations of photochemical and kinetic parameters were published lately [13, 14]. Thus, the conditions appear to be favourable at present for the updating of former reaction mechanisms of the unpolluted troposphere.

In this study, we deal with the elaboration and kinetic analysis of a photochemical mechanism which is intended to describe the chemistry of the "unpolluted troposphere" or more correctly the reactions that occur in a clean lower atmosphere not exposed to the direct perturbation from local emitting sources. We shall call this scheme, which incorporates emission, wet and dry deposition processes, the background model of the troposphere. The first part of the present study deals with the formulation of the model, while the second part reports on a detailed kinetic analysis and reduction of the proposed model by means of sensitivity analysis.

Reaction conditions and rate parameters

The results of calculations derived from a reaction model depend on the concentrations of the reactive species and on the values of the kinetic parameters. Thus, as a first step in establishing our background model, we need to specify the conditions under which the model is to be applied and to indicate the sources of rate parameters that will be used. Regarding the range of applicability, the model should be suitable first of all for the description of the photochemistry of the unpolluted lower troposphere and especially for reproduction of the diurnal variation of the concentrations of reactive species around ground level.

Concentrations of tropospheric constituents

We select concentrations for tropospheric constituents that can be taken as typical ones for the clean air at northern mid-latitudes of 45°N above ground level on an average summer day around noon (zenit angle: $\chi 27^{\circ}$). Such daytime concentrations, given in Table I, were compiled by considering the following sources: (i) Critical evaluation of results of concentration measurements made by Logan *et al.* [10] in the unpolluted atmosphere; (ii) Typical composition of very clean tropospheric air as assumed by Calvert and Stockwell [4]; (iii) Results of tropospheric model calculations at mid-latitudes by Logan *et al.*; (iv) Mixing ratios for sulfur compounds reported by Tiwari and Augustsson [13].

Nocturnal concentrations are also given in Table I. They are intended to be typical for an average summer day at night and were compiled by considering the following sources: (i) Simple empirical estimations; (ii) Results of tropospheric model calculations at mid-latitudes [10].

Table I

Typical concentrations for tropospheric constituents at northern mid-latitudes and surface conditions
(Units are: molecule cm^{-3} . 2.5 E19 designates 2.5×10^{19} , etc.)

Constituents	Concentrations		Constituents	Concentrations	
	day-time	nocturnal		day-time	nocturnal
$\text{N}_2 + \text{O}_2$	2.5 E19	2.5 E19	HONO	3 E6	1 E6
O_2	5.1 E18	5.1 E18	HONO_2	8 E8	7 E8
H_2O	3.8 E17	3.8 E17	HO_2NO_2	1 E7	1 E5
CO	4.0 E12	4.0 E12	O	5 E2	$\sum 1 \text{ E}-5$
CH_4	4.2 E13	4.2 E13	O^*	3 E-3	$\sum 1 \text{ E}-5$
HCHO	4 E9	3 E9	OH	1 E6	1 E2
H_2O_2	1 E10	5 E9	HO_2	3 E8	1 E6
$\text{CH}_3\text{O}_2\text{H}$	5 E9	3 E9	CH_3O_2	8 E7	1 E7
O_3	3 E11	2 E11	CH_3O	1 E-1	1 E-5
NO	8 E8	5 E4	CH_3O	5 E1	5 E-3
NO_2	4 E8	1 E9	SO_2	5 E9	5 E9
N_2O_5	2 E2	1 E7	H_2SO_4	5 E8	1 E8
NO_3	1 E4	1 E8			

Calculation of diurnal variations of constituent concentrations with our background model yielded of course somewhat different concentrations, however, the difference was not as significant as to change any of our conclusions affecting the selection of the reaction mechanism.

Kinetic parameters for thermal and photochemical reactions

Kinetic parameters, for thermal reactions were taken from recent critical compilations [14, 13]. The sources of individual kinetic parameters will be indicated in our background model.

The $J_{i \rightarrow j}$ parameter (s^{-1}) for photochemical step $i + h\nu \rightarrow j$ was calculated from Eq (1):

$$J_{i \rightarrow j}(\lambda, z) = \sum \Phi_{i \rightarrow j}(\lambda) \sigma_i(\lambda) I_{\text{act.}}(\lambda, \chi, z) \quad (1)$$

where $\Phi_{i \rightarrow j}$ is the quantum yield of the photochemical process studied, σ_i is the light absorption cross section (cm^2) of species i and $I_{\text{act.}}(\lambda, \chi, z)$ designates the actinic light intensity ($\text{photons cm}^{-2} \text{s}^{-1}$) which depends on the wavelength λ as well as on the solar zenith angle χ and altitude z . The actinic light intensity was obtained as described by Leighton [16]:

$$I_{\text{act.}}(\lambda, \chi, z) = I_0(\lambda) \exp[-\sigma_a(\lambda, z) \sec \chi] \times \\ \times \{gi \cos \chi + (1-gi \cos \chi) \exp[-(\sigma_m(\lambda, z) + \sigma_p(\lambda, z)) \sec \chi]\} \quad (2)$$

where σ_a , σ_m and σ_p designate the attenuation coefficients for absorption, molecular scattering and particulate diffusion, respectively, gi is a correction term taken as $gi = 1$, and I_0 is the solar flux outside the atmosphere.

Calculating the J parameters according to Eq. (1), the I_0 spectrum was taken from Vernazza *et al.* [17]. The Φ and σ values were obtained from the tables of Baulch *et al.* [13] or in a few cases from other sources [3, 14, 18]. In this way we obtain $J = 6.9 \times 10^{-3} \text{ s}^{-1}$ for the kinetic parameter of reaction



at $\chi = 27^\circ$. This is in excellent agreement with the clear sky values 8.0×10^{-3} — $8.7 \times 10^{-3} \text{ s}^{-1}$ determined experimentally for this reaction under similar ($\chi = 30^\circ$) ambient conditions [19—22]. The difference between our calculated and the experimental values appears indeed small if one considers that we used a very simple approach which does not take into account multiple scattering and assumes zero albedo.

Parameters for emission and deposition processes

Emission and deposition processes are treated in the same way as chemical reactions. Thus, deposition is regarded as a first order process. The rate parameter d is given in s^{-1} unit and the rate of deposition is expressed in $\text{molec. cm}^{-3} \text{ s}^{-1}$ unit (since we use molec. cm^{-3} for concentration). On the other hand, emission is regarded as a zeroth order process. The rate parameter e is given in $\text{molec. cm}^{-3} \text{ s}^{-1}$ units and expresses the rate of input of a pollutant from emission sources into the troposphere at a definite altitude. These e parameters are derived from literature emission data usually given in $\text{g km}^{-2} \text{ year}^{-1}$. In the derivation we do not take into account explicitly diffusion and convection of the emitted primary pollutants. Since the time scale of vertical mixing in the troposphere is short compared to the kinetic lifetime of these species, we proceed as if at all altitudes of the 10 km high troposphere direct input of primary pollutants from emission would occur. Accordingly, it is assumed that input rates used in our model vary with altitude in the same way as the number density of air changes with height.

On a time-scale of years, the composition of the troposphere can be looked upon as constant. This stability of the composition allows us to supplement or correct our insufficient knowledge on emission and deposition data. Namely, for given typical constituent concentrations, the emission and deposition parameters are interrelated in a way that assures the balances in the N-atom, C-atom, and S-atom budgets. Utilizing this inter-connection we have slightly modified some of the emission parameters which were chosen originally on the basis of literature data (see below).

The source considered for methane emission was the CODATA compilation by Baulch *et al.* [13] yielding the parameter (for use at 0 km altitude)

$$e(\text{CH}_4) = 1.5 \times 10^5 \text{ molec. cm}^{-3} \text{ s}^{-1}.$$

From the same literature source we derived 6.5×10^5 molec. $\text{cm}^{-3} \text{s}^{-1}$ for the parameter of carbon monoxide emission. However, the balance of the CO budget required a 40% reduction of the original value, thus finally we accepted

$$e(\text{CO}) = 4.1 \times 10^5 \text{ molec. cm}^{-3} \text{ s}^{-1}.$$

This corresponds roughly to the lower limit of the emission data given in the CODATA compilation.

Three recent values for NO_x background emission can be found in the literature [13, 23, 24] which were all published in the last years. They agree very well and suggest 6.3×10^3 molec. $\text{cm}^{-3} \text{s}^{-1}$ for the rate of NO_x emission. Dividing this in the ratio of one to one between NO and NO_2 we obtain

$$e(\text{NO}) = 3.2 \times 10^3 \text{ molec. cm}^{-3} \text{ s}^{-1}$$

$$e(\text{NO}_2) = 3.2 \times 10^3 \text{ molec. cm}^{-3} \text{ s}^{-1}.$$

Emission data for SO_2 are rather uncertain: Most of the SO_2 emission is of anthropogenic origin, the global distribution of emission sources is inhomogeneous and their strength is varying significantly in time. Using the data reported by Mészáros [25] for the sulfur input into the atmosphere over Europe, we arrive at an emission parameter of 2.3×10^5 molec. $\text{cm}^{-3} \text{s}^{-1}$. The maintenance of the balance in the sulfur budget requires a reduction by a factor of 4, thus we accept

$$e(\text{SO}_2) = 6.0 \times 10^4 \text{ molec. cm}^{-3} \text{ s}^{-1}$$

The deposition parameters are compiled in Table II and a few remarks regarding the origin of the parameters are given in the foot-note of the Table. Only the deposition data of the sulfur compounds need further considerations. From the wet and dry deposition rates of sulfur compounds given for Europe by

Table II

Deposition parameters
(Unit are: s^{-1} . 2.4 E-6 designates 2.4×10^{-6} , etc.)

Species	Wet deposition	Dry deposition	Overall deposition
HONO_2	2.4 E-6 (a)	5.0 E-6 (c)	7.4 E-6
HONO	2.4 E-6 (b)	5.0 E-6 (b)	7.4 E-6
H_2O_2	2.4 E-6 (b)	5.0 E-6 (c)	7.4 E-6
$\text{CH}_3\text{O}_2\text{H}$	2.4 E-6 (b)	5.0 E-6 (b)	7.4 E-6
O_3	— (c)	4.0 E-6 (c)	4.0 E-6
SO_2	8.0 E-7 (d)	6.1 E-6 (d)	6.9 E-6
SO_4^{2-}	7.3 E-6 (d)	6.0 E-7 (d)	7.9 E-6

- (a) Taken from Levine and Schwartz [26];
 (b) Assumed to be the same as the parameters of HONO_2 ;
 (c) Estimated
 (d) See text

Mészáros [25] and from the assumption that sulfur deposition consists mainly of SO_2 and SO_4^{2-} deposition, one obtains the parameters

$$d_{\text{wet}}(\text{SO}_2) + d_{\text{wet}}(\text{SO}_4^{2-}) = 8.1 \times 10^{-6} \text{ s}^{-1}$$

$$d_{\text{dry}}(\text{SO}_2) + d_{\text{dry}}(\text{SO}_4^{2-}) = 6.7 \times 10^{-6} \text{ s}^{-1}.$$

Individual parameters can be derived by utilizing the observation that wet deposition of sulfur compounds consists of about 90% SO_4^{2-} and 10% SO_2 , while there is about 10% SO_4^{2-} and 90% SO_2 contribution to dry deposition. Hence the parameters indicated in Table II were obtained.

The reaction mechanism

The first step in the formulation of the reaction mechanism was the selection of the reacting species. For sake of simplicity, the class of hydrocarbons was represented by a single species, the most abundant hydrocarbon in the "unpolluted" troposphere, i.e. by methane. This decision implied the consequence that products with more than one C-atom (i.e. higher carbonyl compounds, nitrites and nitrates) and the corresponding free radicals were not formed according to the reaction mechanism. All together 36 reacting species were taken into account. Among these were three major atmospheric constituents (O_2 , N_2 , H_2O), twenty-one primary and secondary pollutant molecules and twelve free radical species.

Neglecting very unlikely transformations of the assumed reacting species, still a great number of reactions had to be dealt with. This set of reasonable reactions was reduced by competitive kinetic considerations. Thus, the rates of formation and consumption of the assumed reacting species were calculated at typical tropospheric concentrations and those reactions were neglected which proved to be significant neither at day-time nor at nocturnal conditions. (Systematic calculations were carried out only at surface conditions given in Table I, however, the importance of selected reactions were estimated also at 10 km latitude.)

The use of the competitive kinetic method in the formulation of the background mechanism is demonstrated for the case of nitric acid and triplet oxygen atom reactions in Table III and IV, respectively. In the first part of Table III, the reactions considered as possible HONO_2 forming processes are given. Steps a_1 and a_2 are seen to be the major day-time and nocturnal processes, respectively, while reaction a_3 is of no importance at the conditions studied. Thus, we include steps a_1 and a_2 in the background model and omit reaction a_3 . On the other hand, deposition can be seen to be the dominating HONO_2 removal process at day and night around surface level. However, reactions b_1

Table III

Reaction competition in HONO₂ formation and removal
(Rates in molec. cm⁻³ s⁻¹ units.)

No.	Reaction	day-time	nocturnal
a ₁	OH + NO ₂ + M → HONO ₂ + M	6.4 E3 (190%)	1.6 E0 (0%)
a ₂	N ₂ O ₅ + H ₂ O → 2HONO ₂	2.3 E 1 (0%)	1.1E4 (100%)
a ₃	CH ₃ O ₂ + NO ₂ → HCHO + HONO ₂	≤ 1E 0 (0%)	≤ 1E 0 (0%)
b ₁	HONO ₂ + hν → OH + NO ₂	3.6 E2 (5%)	0 (0%)
b ₂	OH + HONO ₂ → H ₂ O + NO ₂	1.0 E2 (2%)	9.1 E -3 (0%)
b ₃	HONO ₂ → deposition	5.9 E3 (93%)	5.2 E3 (100%)

Table IV

Reaction competition in triplet oxygen atom formation and removal
(Rates in molec. cm⁻³ s⁻¹ units.)

No.	Reaction	day-time
a ₁	NO ₂ + hν → NO + O	2.8 E6 (4%)
a ₂	O ₃ + hν → O + O ₂	6.3 E7 (93%)
a ₃	NO ₃ + hν → NO ₂ + O	1.7 E3 (0%)
a ₄	O* + M → O + M	2.2 E6 (3%)
a ₅	OH + OH → H ₂ O + O	1.9 E0 (0%)
b ₁	O + O ₂ + M → O ₃ + M	3.8 E7 (100%)
b ₂	O + NO + M → NO ₂ + M	1.4 E0 (0%)
b ₃	O + NO ₂ → NO + O ₂	1.5 E0 (0%)
b ₄	O + NO ₂ + M → NO ₃ + M	1 E0 (0%)
b ₅	O + SO ₂ + M → SO ₃ + M	≤ 8.5 E -2 (0%)

and b₂ are of some importance at day-time (as shown in Table III) and they become the main HONO₂ removing processes at high altitudes where UV light intensity is much greater. Thus, all three reactions will be included in the scheme.

Reactions of triplet oxygen atoms are presented in Table IV. (Due to the very low O and O* concentrations and the insignificant rates of photochemical reactions at night, competitive kinetic studies were meaningless at nocturnal circumstances.)

Among the O-atom forming reactions, the contribution of steps a₁, a₂ and a₄ is undoubtedly significant and that of reaction a₃ is negligible. Reaction a₃ is not in fact important from the point of view of O formation, however it is a major step in NO₃ removal. Thus, we include a₁, a₂, a₃ and a₄ in the reaction scheme. Regarding O-atom removal, the ozon formation reaction is the only one which needs to be taken into account.

Table V

Reaction mechanism
Units: (molec., cm³, s)

No.	Reaction	Ref.	Rate coefficient	k
1	2	3	4	5
1	NO ₂ + hν → NO + O	(a)	Altitude and λ dependent	6.9 E-3
2	O + O ₂ + M → O ₃ + M	(c)	$k_0 = 6.9 \times 10^{-34} (T/300)^{-1.25} [\text{O}_2] = 6.2 \times 10^{-34} (T/300)^{-2.00} [\text{N}_2]$ $k_{\infty} = 2.8 \times 10^{-12}$ $F_c = \exp(-T/1800) + \exp(-7200/T)$	1.5 E-14
3	O ₃ + NO → O ₂ + NO ₂	(b)	$k = 2.2 \times 10^{-12} \exp(-1430/T)$	1.8 E-14
4	O ₃ + hν → O* + O ₂	(a)	Altitude and λ dependent	2.0 E-5
5	O ₃ + hν → O + O ₂	(a)	Altitude and λ dependent	2.1 E-4
6	O* + M → O + M	(b)	$k = 2.9 \times 10^{-11}$	2.9 E-11
7	O* + H ₂ O → OH + OH	(b)	$k = 2.2 \times 10^{-10}$	2.2 E-10
8	OH + NO + M → HONO + M	(c)	$k_0 = 6.5 \times 10^{-31} (T/300)^{-2.4} [\text{M}]$ $k_{\infty} = 1.0 \times 10^{-11}$ $F_c = \exp(-T/1300) + \exp(-5200/T)$	5.0 E-12
9	HONO + hν → OH + NO	(a)	Altitude and λ dependent	1.4 E-3
10	OH + NO ₂ + M → HONO ₂ + M	(c)	$k_0 = 1.8 \times 10^{-30} (T/300)^{-2.9} [\text{O}_2] = 2.6 \times 10^{-30} (T/300)^{-2.9} [\text{N}_2]$ $k_{\infty} = 3.5 \times 10^{-11}$ $F_c = \exp(-T/840) + \exp(-3360/T)$	1.6 E-11
11	HONO ₂ + hν → OH + NO ₂	(a)	Altitude and λ dependent	4.5 E-7
12	OH + HONO ₂ → H ₂ O + NO ₂	(b)	$k = 9.4 \times 10^{-12} \exp(778/T)$	1.3 E-13
13	OH + CO ₂ → HO ₂ + CO ₂	(b)	$k = 1.5 \times 10^{-13} (1 + 0.70 P_{\text{atm}}) / (1 + 0.17 P_{\text{atm}})$	2.2 E-13
14	HO ₂ + NO → OH + NO ₂	(b)	$k = 3.7 \times 10^{-12} \exp(240/T)$	8.3 E-12
15	HO ₂ + NO ₂ → HONO + O ₂	(b)	$k \leq 1 \times 10^{-16}$	≤ 1 E-15
16	HO ₂ + NO ₂ + M → HO ₂ NO ₂ + M	(c)	$k_0 = 2.1 \times 10^{-9} (T/300)^{-5} [\text{M}]$ $k_{\infty} = 5.0 \times 10^{-12}$ $F_c \approx 0.4$	1.0 E-12
17	HO ₂ NO ₂ + M → HO ₂ + NO ₂ + M	(c)	$k_0 = 5.0 \times 10^{-6} \exp(-10000/T) [\text{M}]$ $k_{\infty} = 3.5 \times 10^{14} \exp(-10420/T)$ $F_c \approx 0.4$	5.4 E-2
18	HO ₂ NO ₂ + hν → OH + NO ₂	(c)		

18	$\text{HO}_2\text{NO}_2 + h\nu \rightarrow \text{OH} + \text{NO}_2$	(a)	Altitude and χ dependent	5.8 E-6
19	$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	(e)	$k = 4.0 \times 10^{-11}$	4.0 E-11
20	$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	(b)	$k = 1.6 \times 10^{-12} \exp(-940/T)$	6.8 E-14
21	$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$	(b)	$k = 1.4 \times 10^{-14} \exp(-580/T)$	2.0 E-15
22	$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	(b)	$k = 1.2 \times 10^{-12} \exp(-2450/T)$	3.2 E-17
23	$\text{NO}_3 + h\nu \rightarrow \text{NO} + \text{O}_2$	(a)	Altitude and χ dependent	2.0 E-2
24	$\text{NO}_3 + h\nu \rightarrow \text{NO}_2 + \text{O}$	(a)	Altitude and χ dependent	1.7 E-1
25	$\text{NO} + \text{NO}_3 \rightarrow \text{NO}_2 + \text{NO}_2$	(b)	$k = 8 \times 10^{-12} \exp(250/T)$	1.9 E-11
26	$\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2$	(b)	$k = 2.5 \times 10^{-14} \exp(-1230/T)$	4.0 E-16
27	$\text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M}$	(c)	$k_0 = 3.7 \times 10^{-20} (T/300)^{-4.1} [\text{M}]$ $k_{300} = 1.6 \times 10^{12} (T/300)^{0.2}$ $F_C = \exp(-T/250) + \exp(-1050/T)$	1.2 E-12
28	$\text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M}$	(c)	$k_0 = 2.2 \times 10^{-2} (T/300)^{-4.4} \exp(-11080/T) [\text{M}]$ $k_{300} = 9.7 \times 10^{10} (T/300)^{0.1} \exp(-11080/T)$ $F_C = \exp(-T/250) + \exp(-1050/T)$	5.2 E-2
29	$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HONO}_2$	(d)	$k = 9 \times 10^{-19}/T$	3 E-21
30	$\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$	(c)	$k = 2.4 \times 10^{-12} \exp(-1710/T)$	7.7 E-15
31	$\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M}$	(c)	$k_0 = 2.6 \times 10^{-31} (T/300)^{-3.0} [\text{M}]$ $k_{300} = 2 \times 10^{-12}$ $F_C = \exp(-T/360) + \exp(-1440/T)$	8.1 E-13
32	$\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2$	(b)	$k = 4.2 \times 10^{-12} \exp(180/T)$	7.6 E-12
33	$\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2$	(b)	$k = 1.0 \times 10^{-13} \exp(-1300/T)$	1.3 E-15
34	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow 2\text{CH}_3\text{O} + \text{O}_2$	(c)	$k = 1.5 \times 10^{-13}$	1.5 E-13
35	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{HCHO} + \text{CH}_3\text{OH} + \text{O}_2$	(c)	$k = 2.2 \times 10^{-13}$	2.2 E-13
36	$\text{OH} + \text{HCHO} \xrightarrow{\text{O}_2} \text{H}_2\text{O} + \text{HO}_2 + \text{CO}$	(b)	$k = 1.1 \times 10^{-11}$	1.1 E-11
37	$\text{HCHO} + h\nu \xrightarrow{\text{O}_2} \text{HO}_2 + \text{HO}_2$	(a)	Altitude and χ dependent	2.0 E-5
38	$\text{HCHO} + h\nu \rightarrow \text{H}_2 + \text{CO}$	(a)	Altitude and χ dependent	4.3 E-5
39	$\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{O}_2\text{H} + \text{O}_2$	(c)	$k = 7.7 \times 10^{-14} \exp(1300/T)$	6.1 E-12
40	$\text{CH}_3\text{O}_2\text{H} + h\nu \rightarrow \text{CH}_3\text{O} + \text{OH}$	(c)	Altitude and χ dependent	6.4 E-6
41	$\text{OH} + \text{CH}_3\text{O}_2\text{H} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{O}_2$	(c)	$k = 2.9 \times 10^{-12} \exp(-160/T)$	1.7 E-12

(Table V continued)

No.	Reaction	Ref.	Rate coefficient	
			3	4
1				4
2				5
42	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	(b)	$k = (3.4 + 2.5 P_{\text{atm}}) \times 10^{-14} \exp(1150/T)$	2.8 E-12
43	$\text{HO}_2 + \text{HO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{H}_2\text{O}$	(b)	$k = 2.2 \times 10^{-32} \exp(5800/T)$	6.2 E-30
44	$\text{H}_2\text{O}_2 + h\nu \rightarrow \text{OH} + \text{OH}$	(a)	Altitude and λ dependent	7.8 E-6
45	$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	(b)	$k = 3.1 \times 10^{-12} (\exp - 187/T)$	1.7 E-12
46	$\text{OH} + \text{SO}_2 + \text{M} \xrightarrow{\text{O}^{\cdot}, \text{H}^{\cdot}, \text{O}} \text{H}_2\text{SO}_4 + \text{HO}_2$	(c)	$k_0 = 3.0 \times 10^{-31} (T/300)^{-2.9} [\text{M}]$ $k_{\infty} = 2.5 \times 10^{-12}$ $F_C = 0.55$	1.1 E-12
47	$\text{HO}_2 + \text{SO}_2 \xrightarrow{\text{H}_2\text{O}} \text{OH} + \text{H}_2\text{SO}_4$	(b)	$k \leq 1 \times 10^{-15}$	$\leq 1 \text{ E-18}$
48	$\text{CH}_3\text{O}_2 + \text{SO}_2 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{O} + \text{H}_2\text{SO}_4$	(b)	$k \leq 5 \times 10^{-17}$	$\leq 5 \text{ E-17}$
49	$\text{HONO}_2 \rightarrow$ deposition	(f)	Altitude dependent	7.4 E-6
50	$\text{HONO} \rightarrow$ deposition	(f)	Altitude dependent	7.4 E-6
51	$\text{H}_2\text{O}_2 \rightarrow$ deposition	(f)	Altitude dependent	7.4 E-6
52	$\text{CH}_3\text{O}_2\text{H} \rightarrow$ deposition	(f)	Altitude dependent	7.4 E-6
53	$\text{O}_3 \rightarrow$ deposition	(f)	Altitude dependent	4.0 E-6
54	$\text{SO}_2 \rightarrow$ deposition	(f)	Altitude dependent	6.9 E-6
55	$\text{SO}_4^{\cdot-} \rightarrow$ deposition	(f)	Altitude dependent	7.9 E-6
56	emission \rightarrow NO	(f)	Altitude dependent	3.2 E 3
57	emission \rightarrow NO ₂	(f)	Altitude dependent	3.2 E 3
58	emission \rightarrow CH ₄	(f)	Altitude dependent	1.5 E 5
59	emission \rightarrow CO	(f)	Altitude dependent	4.1 E 5
60	emission \rightarrow SO ₂	(f)	Altitude dependent	6.0 E 4

(a) J parameters calculated from Φ and σ values and solar intensities (see text);

(b) Kinetic parameters from Atkinson and Lloyd [14];

(c) Kinetic parameters from Baulch et al. [13];

(d) k from Atkinson et al. [3];(e) k from Logan et al. [10];

(f) Emission and deposition parameters derived from literature source (see text).

As a result of our kinetic considerations the number of reacting species and reactions could be decreased considerably. We omitted species like CH_3ONO , CH_3ONO_2 , $\text{CH}_3\text{O}_2\text{NO}_2$ and CH_2OO . Furthermore, the very reactive species H , CHO , HOSO_2 and SO_3 , which disappear in fast processes, were not dealt with explicitly; they were eliminated by amalgamating the formation and removal reactions. Finally, the products H_2 , CO_2 and CH_3OH were treated as inert species with no significant removal reactions. Thus, apart from the major atmospheric constituents O_2 , N_2 and H_2O , we have all together 22 reactive species. Their reactions — including emission and deposition processes — form the 60 step background mechanism presented in Table V. The rate expressions, their sources and the rate coefficients for $\chi = 27^\circ$, surface conditions and 298 K (last column) are also given in the Table.

Diurnal variation of tropospheric constituent concentrations

The reaction model presented in Table V has been used to calculate the diurnal concentration profiles for tropospheric trace pollutants. Calculations were carried out for average climatological conditions intended to simulate a typical summer day at mid-latitudes of 45°N (298 K temperature) at 0 km altitude.

The system of kinetic differential equations was solved using a fourth order Runge—Kutta integration routine of Gottwald and Wanner [28]. The concentrations of the species characterized by very short kinetic lifetimes (i.e. O , O^* , OH , CH_3 and CH_3O) were obtained from steady state expressions.

The initial concentrations chosen were the day-time data given in Table I. The J parameters of the photochemical processes were allowed to change in a manner simulating the diurnal variation of insolation. Calculations were continued for a simulated 12 days period. The profiles calculated in succession were compared and it was found that the results obtained after about the fifth simulated day were in good agreement with each other. The total changes in the concentrations were not large; the final results read from the calculated profiles at noon and at night agreed in all cases within a factor of 3 with the initial concentrations given in Table I. The very good agreement between calculated results and literature data (that include concentration measurements made in the troposphere) shows our model to be internally consistent and supports the reaction mechanism and the kinetic parameters used in our background model.

The computed diurnal variations of the trace constituents of the troposphere are presented in Figs 1—3.

The computed concentration patterns for nitrogen containing species are shown in Fig. 1. As expected, HONO_2 and NO_2 are the most abundant species

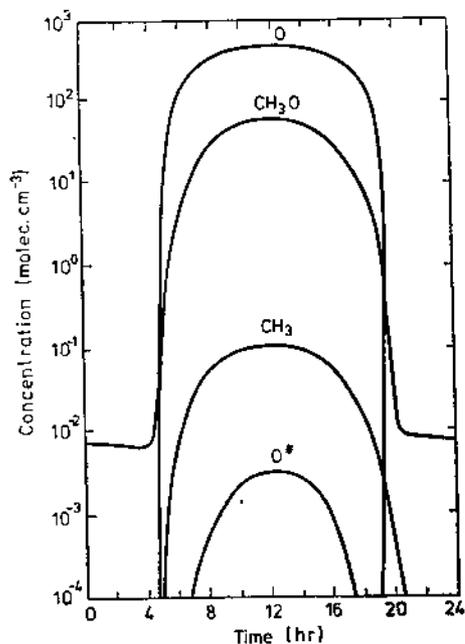


Fig. 1. Diurnal variation of concentrations of nitrogen containing constituents at northern mid-latitudes (45°N) above ground level

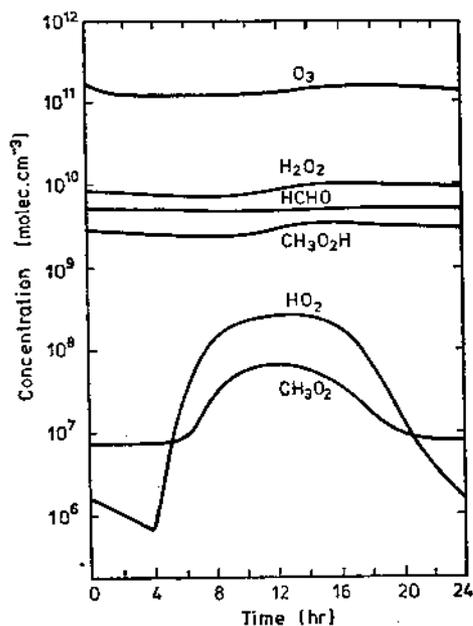


Fig. 2. Diurnal variation of concentrations of oxygen containing species at northern mid-latitudes (45°) above ground level

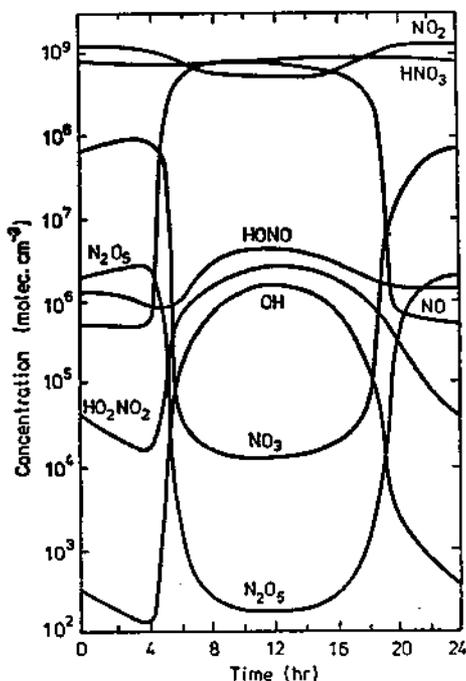


Fig. 3. Diurnal variation of concentrations of short lived transient species at northern mid-latitudes (45°N) above ground level

and the concentration of NO becomes comparable to these during the sunlit period of the day. There is a significant increase observable in NO concentration immediately after sunrise and the opposite occurs at sunset. This may be explained by taking into account that NO_2 photolysis is the predominant route of NO formation and consequently sudden changes in NO formation occur at the setting in and at the termination of insolation.

The opposite behaviour is observed for NO_3 and for N_2O_5 of which NO_3 is the main precursor: These concentrations decrease at sunrise and increase at sunset. The sudden changes are caused by the commencement and termination of NO_3 photolysis.

The most important species in tropospheric photochemistry — the driving force of the photooxidation process — is the OH radical. Its concentration is seen to change four orders of magnitude during the day; most of it is occurring again at sunrise and sunset. The OH concentration attains a maximum at noon. The computed maximum value is 1.5×10^6 molec. cm^{-3} , which compares favourably with the results of ambient measurements. From observations made at Jülich, West Germany (51°N) on sunny days in summer 1979 between 11.00 and 15.00 hours an average value of $(1.7 \pm 3) \times 10^6$ OH molec. cm^{-3} was

derived. Under similar conditions in 1980 similar results were obtained, with most values between 1 to 2×10^6 OH molec. cm^{-3} [29].

Important oxidizing constituents of the troposphere are the species HO_2 , CH_3O_2 and O_3 whose computed diurnal concentration patterns are presented in Fig. 2. Compared with OH, the HO_2 and CH_3O_2 species decay slower, while O_3 concentration undergoes only moderate changes during the diurnal period. The different concentration patterns result from the different fate of the reacting species: OH reacts predominantly with CO and CH_4 , while the oxidants are consumed in reactions with each other and especially in reactions with NO.

The diurnal concentration profiles of some transient species are shown in Fig. 3. These four free radicals together with OH represent a class of species which are characterized by very short kinetic lifetimes. Their tropospheric lifetimes are well below 1 s and the variation of the concentrations follows closely the changes in the ambient conditions, particularly changes in insolation, as it appears from the results presented in the figure.

Results of diurnal concentration profile computations show that the background model developed in this paper gives a reliable account of the important aspects of the photochemistry of the troposphere.

It is expected from the detailed kinetic analysis of the mechanism—which will be reported on in Part II—to reveal the reactions that play important role in the photooxidation processes and to select those reactions which are of little significance in tropospheric photochemistry.

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